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The Synthesis and Properties of Picryldinitrobenzimidazoles and the "Trigger Linkage" in Picryldinitrobenzotriazoles

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FOREWORD

1-(2',4',6'-Trinitrophenyl)-5,7-dinitrobenzotriazole (BTX) is a heat resistant initiating explosive; preliminary tests indicate this material owes its impact sensitivity to the N=N-N-picryl functional grouping. This report describes the synthesis, structural characterization, and explosive properties of some related 1-(2',4',6'-trinitrophenyl)benzimidazoles which confirm that the N=N-N-picryl moiety contains the "trigger linkage" in BTX. It is suggested that insensitive explosives may be obtained by avoiding this N=N-N-picryl functionality.

This report has been reviewed for technical accuracy by Richard A. Hollins.

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The synthesis of certain picryldinitrobenzimidazoles and their structural elucidation are described. Their explosive properties are discussed and compared with those of the corresponding benzotriazoles. These comparisons allow the identification of the Pic-N-N=N moiety as the "trigger linkage" in impact initiation of picrylbenzotriazoles. Implications of this result on the design and synthesis of new polynitroheterocycles as energetic materials are also discussed.

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CONTENTS

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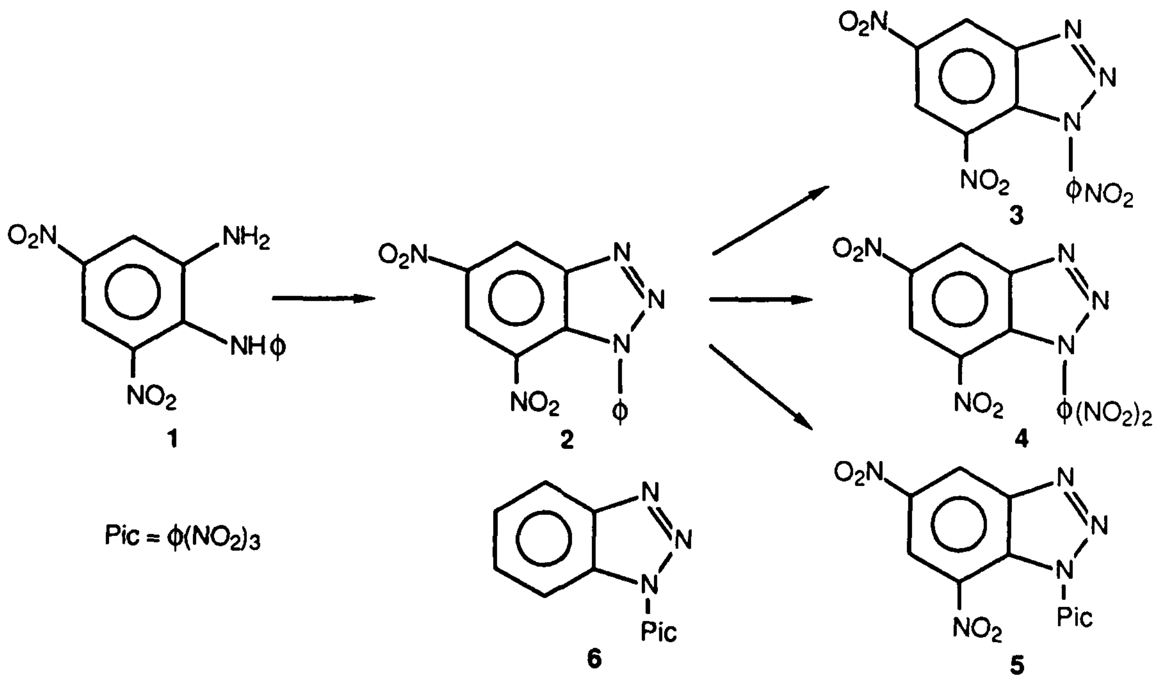
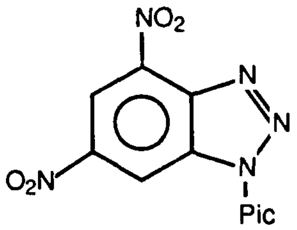
INTRODUCTION

During efforts directed toward the synthesis of highly nitrated diphenylamines, desired as potential new dense energetic materials and for structure/property correlations, attempted nitration of 2-phenylamino-3,5-dinitroaniline (**1**) with nitric acid in acetic acid at ambient temperature gave 1-phenyl-5,7-dinitrobenzotriazole (**2**) in high yield. Further, nitration of **2** under progressively more vigorous conditions afforded 1-(4'-nitrophenyl)-, 1-(2',4'-dinitrophenyl)-, and 1-(2',4',6'-trinitrophenyl)-5,7-dinitrophenylbenzotriazole (1-picryl-5,7-dinitrobenzotriazole), (**3**), (**4**), and (**5**), respectively (Reference 1). This latter compound has also been prepared by nitration of 1-(2',4',6'-trinitrophenyl)-benzotriazole (1-picrylbenzotriazole) (**6**) and has found use as a heat resistant initiating explosive under the name BTX (Reference 2). This compound is thermally stable below its melting point of 258°C, has a density of 1.74 (calculated 1.81 (Reference 3)), has a calculated velocity of detonation 7370 m/s and detonation pressure of 232 kbar (Reference 4), and has an impact sensitivity comparable with pentaerythritoltetranitrate (PETN).



Taking advantage of this unexpected synthetic route to benzotriazoles, the impact sensitivity of a series of these compounds was then examined using the Australian version of the Rotter Impact Test. In this test the sample is confined in an anvil/cup arrangement. The criterion used to determine explosion on impact is the evolution of gas, and the result is expressed as the Figure of Insensitivity (F of I), relative to a standard sample of RDX to which is assigned a value of 80 (References 1 and 5). These results, presented in Table 1, led us to the conclusion that BTX (**5**) owes its sensitivity to the N=N-N-Pic moiety rather than to the other portion of the molecule. Thus, the compounds **2** through **5** show a steady increase in sensitivity with increasing nitration of the pendant phenyl ring, parallelling the increase in oxygen balance. The isomeric 1-picryldinitrobenzotriazoles (**7**) and (**8**) show sensitivities similar to that of BTX, the relatively minor differences being attributable to the degree of steric crowding in the molecule. However, 1-picrylbenzotriazole (**6**) also shows a similar impact sensitivity (indeed it appears to be slightly <u>more</u> sensitive than BTX). This value may be compared with that for the isomeric 1-(4'-nitrophenyl)-5,7-dinitrobenzotriazole (**3**), and it becomes apparent that the impact sensitivity of these compounds does not simply parallel the oxygen balance of the whole molecule, but is associated with the picryltriazole segment (Reference 1).



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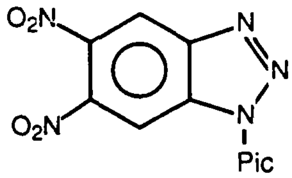

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TABLE 1. Impact *Sensitivity of Benzotriazoles* and Benzimidazoles.

Explosive	Impact sensitivity	
	Rotter F of I (vs RDX = 80)	Bureau of Mines, cm
2	>200	. . .
3	150	. . .
4	120	. . .
5	30	27, 35[a]
6	20-40[b]	11
7	60	40[a]
8	40[b]	35[a]
9	. . .	158

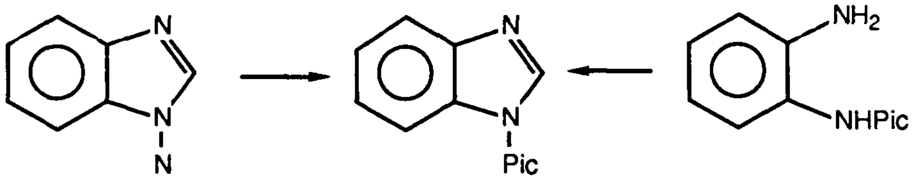
[a] Results from Reference 2.

[b] Restricted quantity of sample.

In order to confirm the hypothesis that the N=N-N-Pic moiety--and the <u>whole</u> N=N-N-Pic moiety rather than simply the N-Pic functionality--provides the "trigger linkage" (Reference 6) for initiation on impact, it was determined to prepare and test various 1-(2',4',6',-trinitrophenyl)benzimidazoles (1-picryl-benzimidazoles) and examine their impact sensitivities. If this structure/sensitivity relationship holds correct and if other properties prove to be attractive, this class of compounds may also provide a new source of insensitive explosives.

RESULTS AND DISCUSSION

1-(2',4',6'-Trinitrophenyl)benzimidazole (**9**) was prepared both by reaction of picryl chloride with benzimidazole and by condensation of picryl chloride with *o*-phenylenediamine followed by cyclization with formic acid or trimethylorthoformate. The impact sensitivity of **9** was measured using a Bureau of Mines machine, the Type 12 tool, and a 2.5 kg drop weight. This result, together with those obtained on the B of M machine for the benzotriazoles, is also presented in Table 1. It may be seen that the 1-picrylbenzimidazole (**9**) has a sensitivity of 158 cm, which may be compared with a value of 11 cm for 1-picrylbenzotriazole (**6**). This clearly supports the hypothesis that the whole N=N-N-Pic moiety comprises the trigger linkage.



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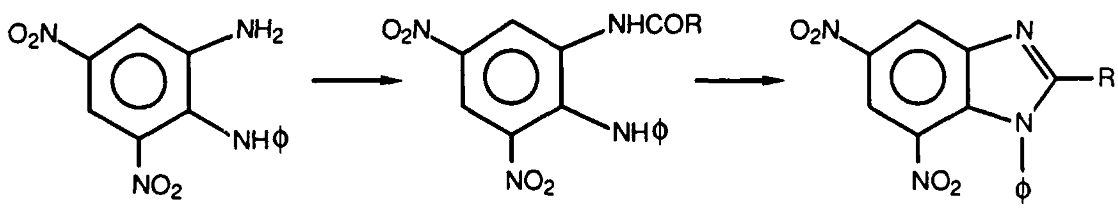
These results made efforts to synthesize 1-picryldinitrobenzimidazoles seem attractive, since such compounds are likely to be very insensitive explosives. A rather naive attempt was made to protect the amine function(s) in **1** by acylation prior to the nitration process. However, reaction of **1** with acetic anhydride in acetic acid gave 1-phenyl-2-methyl-5,7-dinitrobenzimidazole (**11b**), while reaction with formic acid or trimethylorthoformate gave 1-phenyl-5,7-dinitrobenzimidazole (**11a**). Reaction of **1** with trifluoroacetic anhydride indeed gave the desired amide (**10c**), but treatment with either formic or sulfuric acid resulted in dehydration to give 1-phenyl-2-trifluoromethyl-5,7-dinitrobenzimidazole (**11c**). We assume that the amides (**10a**) and (**10b**) were also formed initially, but that dehydration and cyclization to the corresponding benzimidazoles occurred under the conditions of reaction.

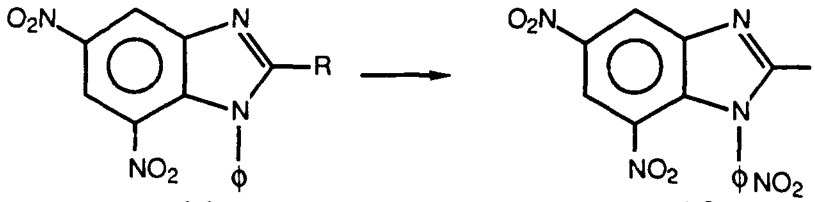


1 **10** **11**

a R = H; **b** R = CH_3; **c** R = CF_3

However, efforts at nitration of the phenyl substituent provided another surprise. Benzimidazole is a slightly weaker acid (pKa 12.3; pKb 5.53) than benzotriazole (pKa 8.57; pKb 1.6 (Reference 7)), suggesting that the benzimidazoyl functionality is somewhat less electronegative. Expectations that nitration of **11a** and **b** should be, if anything, easier than nitration of the benzotriazole analogue (**2**) proved to be false. Nitration of **2** using 70% nitric acid heated under reflux gave the mononitro compound

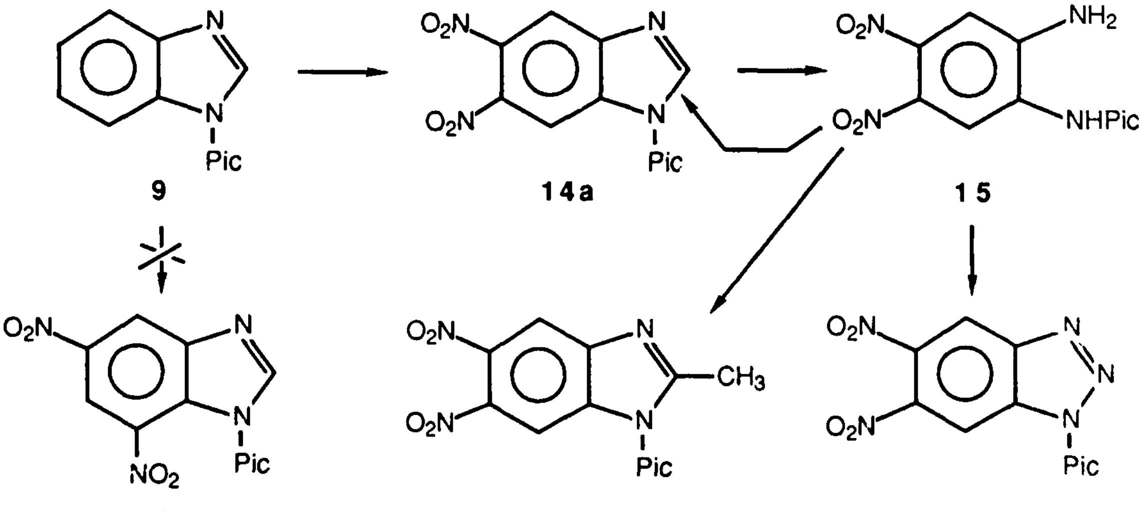
(**3**), whereas the corresponding (**12a**) required nitration of **11a** in 100% nitric acid and 96% sulfuric acid heated under reflux. More forcing conditions led simply to extensive decomposition and no reaction product was isolable. Nitration of the 2-methyl compound (**11b**) gave exactly analogous results.



11 **12**

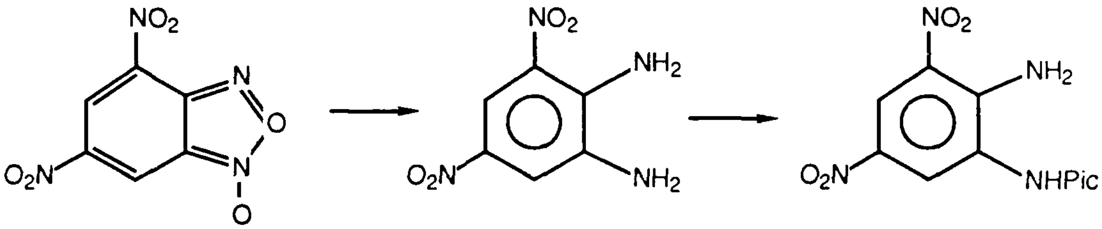
a R = H; **b** R = CH_3

Since **5** can also be prepared by nitration of the benzotriazole portion of **6** (Reference 2), efforts were next directed towards nitration of 1-picrylbenzimidazole (**9**). Nitration of **9** occurred in a mixture of 100% nitric acid and 96% sulfuric acid under reflux. However, the product was not the expected 1-picryl-5,7-dinitrobenzimidazole (**13**), but rather the 5,6-dinitro compound (**14a**), showing again the different behavior of benzimidazoles to electrophilic substitution. Further, **14a** proved to be hydrolytically unstable, decomposing to the amine (**15**) under the conditions of work up. The structure of **15** was confirmed by treatment with nitrous acid to give 1-picryl-5,6-dinitrobenzotriazole (**8**) (Reference 1) and by reaction with acetic anhydride in acetic acid to give the stable 1-picryl-2-methyl-5,6-dinitrobenzimidazole (**14b**). Reaction of **15** with trimethylorthoformate regenerated **14a**, but this product could not be rendered free of the amine either by recrystallization or by chromatography. No effort was made to examine the explosive properties of this material.



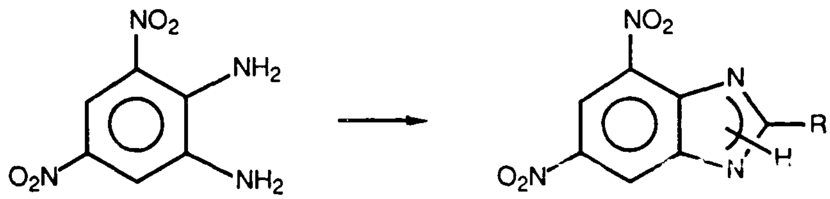
12a **14b** **8**

Having failed in two potential routes to picryldinitrobenzimidazoles, a third approach presented itself, namely cyclization of a preformed *N*-picryl-dinitro-*o*-phenylenediamine to generate the benzimidazole unit. 4,6-Dinitrobenzofuroxan (**16**) may be reduced with hydroiodic acid to generate 3,5-dinitro-1,2-diaminobenzene (**17**) (Reference 8), which was condensed with picryl chloride to yield 2-amino-2',3,4',5,6'-pentanitrodiphenylamine (**18**) (Reference 2). However, this material proved impervious to reaction with trimethylorthoformate, formic acid, or acetic anhydride in acetic acid, and formation of the benzimidazoles was unsuccessful.



16 **17** **18**

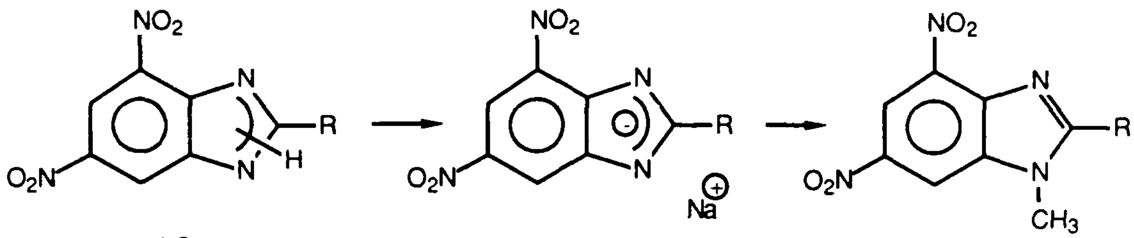
Yet another approach was to couple a preformed dinitrobenzimidazole with a picryl halide. 3,5-Dinitro-1,2-diaminobenzene (**17**) reacts with formic acid under reflux to give 4,6- or 5,7-dinitrobenzimidazole (**19a**), while reaction with acetic anhydride in acetic acid gave the corresponding 2-methyl compound (**19b**). Note that the position of the imidazole proton could not be determined unequivocally.



17 **19**

a R = H; **b** R = CH_3

The dinitrobenzimidazoles (**19a** and **b**) were easily methylated by formation of the sodium salt (by treatment with sodium hydride) followed by treatment with methyl iodide. In each case two positional isomers are possible, but only one product was detected. The product from **19a** was identified as **20a** on the basis of ^{1}H-nuclear magnetic resonance (NMR) experiments, and the product from **19b** was identified as **20b** by analogy and by spectral comparison. In particular, nuclear Overhauser experiments (n.O.e.) showed a comparable enhancement between the methyl group and both the imidazole proton and one of the protons (that resonating at lower field) on the benzo-fused ring, but not with that resonating at higher field. This result indicates that the two protons are at a very similar distance from those on the methyl group--and the downfield proton clearly has to be in the 7-position. This conclusion identifies **19a** as the reaction product and also allows positive assignment of the ^{1}H-NMR spectrum as shown in Table 2. It should be noted that **20a** and **b** are, of course, the products expected to be favoured on steric grounds from the methylation of the intermediate sodium salts.



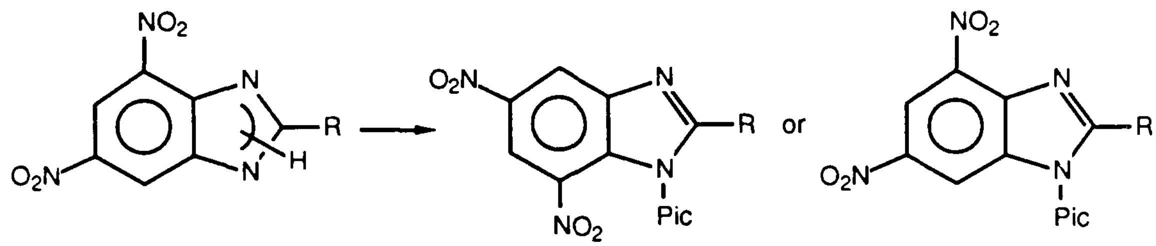
19 → 20

a R = H; **b** R = CH_3

TABLE 2. ^{1}H-Chemical Shifts of Benzimidazoles.

Compound	H_7	H_5	H_2	$H_{3',5'}$	2-CH_3	1-CH_3
19a	8.957		8.673	...	...	...
20a	8.942	8.844	8.669	...	...	4.208
	$J_{5,7}$ = 2.07 Hz					J = 0.38Hz
21a	8.996	8.559	8.981	9.512	...	...
	$J_{5,7}$ = 2.05 Hz					
19b	8.867	8.753	...	...	2.727	...
	$J_{5,7}$ = 2.02 Hz					
20b	8.791		...	...	2.754	4.073
21b	8.927	8.666	...	9.551	2.663	...
	$J_{5,7}$ = 2.08 Hz					

The dinitrobenzimidazole (**19a**) was found to react with picryl fluoride or picryl chloride in either dimethylformamide (DMF) or dimethylsulfoxide (DMSO) solution at ambient temperature. The reaction product (also formed by reaction of picryl fluoride with the sodium salt of **19a**) is clearly a picryldinitrobenzimidazole, as evidenced by the infrared (IR), NMR, and mass spectra. However, it could reasonably be either of the positional isomers (**13a**) or (**21a**), although the latter would certainly appear to be more probable on both steric and electronic grounds, particularly in light of the results of methylation experiments described above. The methyldinitrobenzimidazole (**19b**) reacted with picryl fluoride in DMF at room temperature to give an analogous product.



19 **13** **21**

a R = H; **b** R = CH_3

The structures of the reaction products were ultimately assigned as **21a** and**b** on the basis of NMR spectral evidence (variable temperature, n.O.e., and ^{13}C and ^{1}H coupling experiments), analogy with the products of N-methylation of the dinitrobenzimidazoles, and X-ray crystallography. The ^{1}H-NMR spectra of **19a** and **b**, **20a** and **b** and **21a** and **b** in d_6-acetone solution are presented in Table 2. The remarkable consistency of chemical shifts and coupling constants is clearly indicative of close structural similarity. (Note that the spectra of d_6-DMSO solutions show parallel similarities.) Since the structure of **20a** has already been established by n.O.e. difference experiments, the structures of the other compounds are suggested by analogy. This proposal is supported by the similarities in the ^{13}C-NMR spectra of these compounds shown in Table 3, and by ^{13}C and ^{1}H coupling experiments which assisted in assignment of chemical shifts.

TABLE 3. ^{13}C Chemical Shifts of Benzimidazoles.

Chemical shift	Compound			
	20a	**21a**	**20b**	**21b**
C_2	153.21	151.55	160.05	161.39
C_4	139.94	139.88	139.60	137.69
C_5	113.43	113.81	112.21	112.67
C_6	142.81	144.72	141.91	142.42
C_7	114.64	116.39	114.42	115.50
C_{1a}	138.30	138.53	137.69	136.91
C_{3a}	141.47	141.13	140.91	139.87
C_{P1}	...	127.65	...	125.03
$C_{P2,6}$	...	149.42	...	147.68
$C_{P3,5}$	...	126.33	...	126.02
C_{P4}	...	149.96	...	148.93
2-CH_3	...	...	14.28	14.10
1-CH_3	32.44	...	31.41	...

During investigation of the ^{1}H-NMR spectrum of **21b** in d_6-DMSO, the spectrum changed with changing temperature. In particular, the AB quartet for the aromatic protons 5 and 7 collapsed to a singlet. On closer examination we found that the low field signal attributed to H_7 moved upfield at the rate of about 1.00×10^{-3} ppm/°C, compared with upfield movement of the proton 5 and the picryl protons of 0.15 and 0.49×10^{-3} ppm/°C, respectively. Examination of the ^{1}H-NMR spectrum of **21a** at varying temperatures showed a similar phenomenon, with H_7 decreasing at 0.92×10^{-3} ppm/°C, while H_5, H_2, and the picryl protons decreased at only 0.15, 0.54 and 0.39×10^{-3} ppm/°C, respectively. Initially, it was thought that this more rapid upfield shift might be due to the influence of the picryl group and its easier rotation at higher temperatures, but **20a** was found to behave in the same fashion, H_7 moving upfield at 0.68×10^{-3} ppm/°C, compared with values of 0.19 and 0.47×10^{-3} ppm/°C for H_5 and H_2. However, whatever the reason for this behavior, the similarities between the three compounds again point to the probability of very similar structures. This dependence of chemical shift on temperature is illustrated in Figure 1.

Final NMR evidence for the structure of the benzimidazoles came from a n.O.e. experiment on **21a**, which showed a positive n.O.e. between the picryl protons and both H_2 and H_7, but <u>not</u> H_5. Once again this result is consistent with the structure **21a** but not **13a**.

Crystals of **21a** suitable for single crystal X-ray structure determination could not be prepared. On the other hand, the methyl derivative **21b** proved much more amenable to crystallization in a suitable form. Recrystallization from ethanol/acetone gave two strikingly different crystalline forms, in approximately equal amounts, which were separated by hand. Form I appeared as orange-brown colored, triangular-shaped tabular platelets; form II occurred as cream-yellow six-sided rods. All spectroscopic evidence indicated that the molecular species was the same in each form, thus suggesting the possibility of polymorphism.

Single crystal X-ray structures were determined on each form, confirming in each case the atomic connectivity of **21b**. The structure of form I is illustrated in Figure 2, which also shows the atom numbering used for both forms. Note that the structure is labelled according to crystallographic convention rather than International Union of Pure and Applied Chemistry (IUPAC) rules, and that this numbering system is used throughout the following discussion of single crystal X-ray structure results. Bond lengths and bond angles for forms I and II are listed in Tables 4 and 5, respectively.

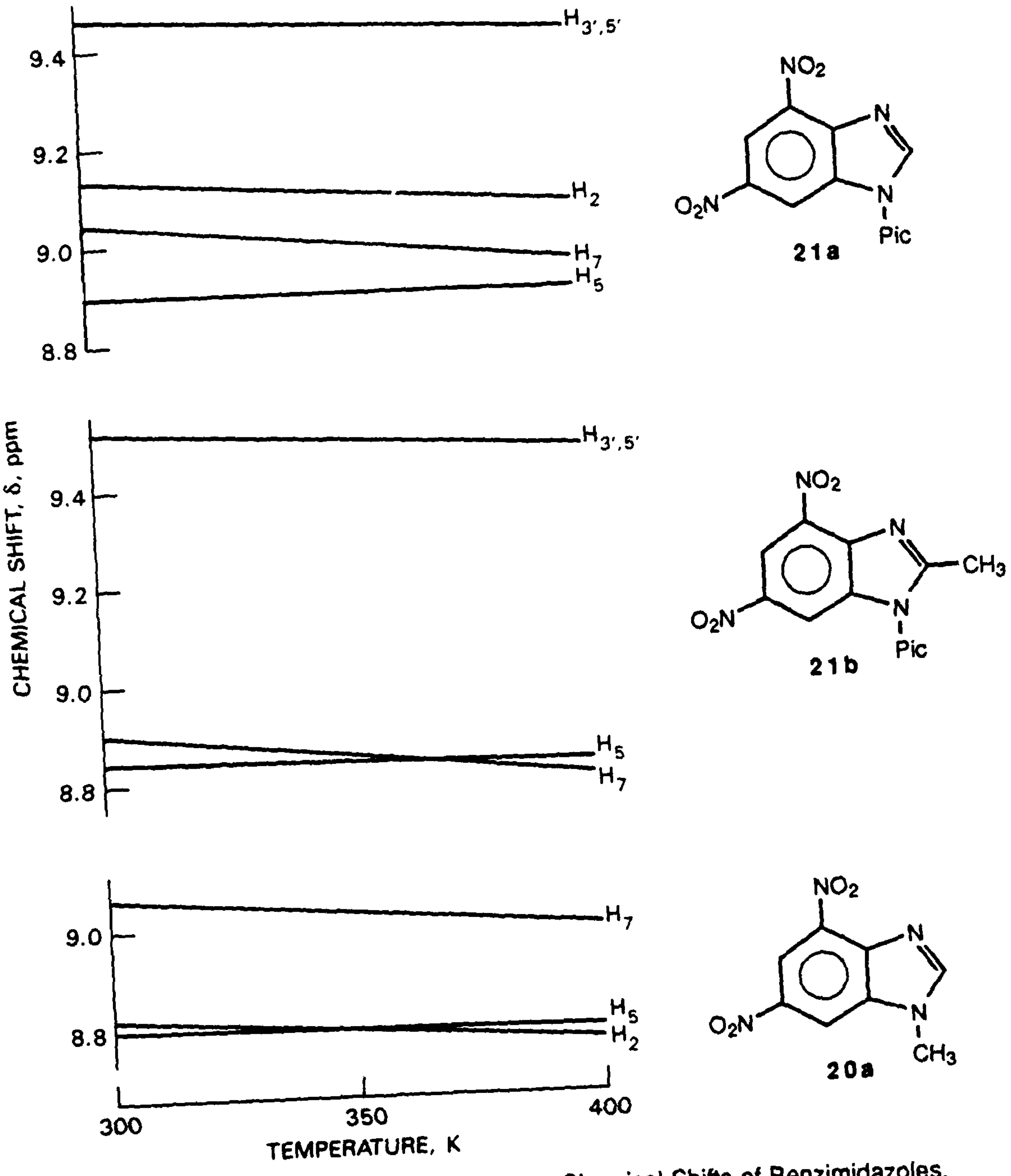


FIGURE 1. Influence of Temperature on Chemical Shifts of Benzimidazoles.

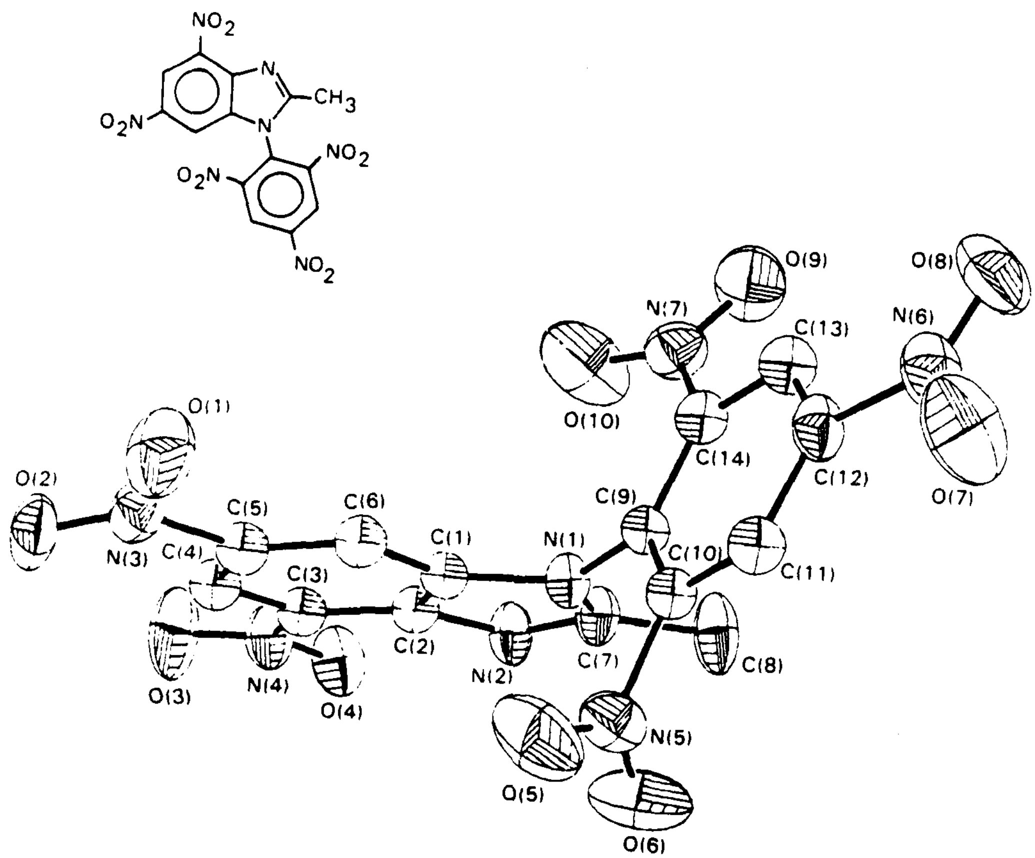


FIGURE 2. Crystal Structure of **21b**, Form I, Plotted with 50% Probability Thermal Ellipsoids and Spheres.

TABLE 4. Bond Lengths, Å, and Bond Angles, deg, for **21b**, Form I.

Bond	Length, Å	Bond	Length, Å
C(1)-C(2)	1.400(5)	C(1)-C(6)	1.391(4)
C(1)-N(1)	1.392(4)	C(2)-C(3)	1.396(4)
C(2)-N(2)	1.386(4)	C(3)-C(4)	1.383(5)
C(3)-N(4)	1.456(5)	C(4)-C(5)	1.380(5)
C(5)-C(6)	1.376(4)	C(5)-N(3)	1.462(4)
C(7)-C(8)	1.494(5)	C(7)-N(1)	1.370(4)
C(7)-N(2)	1.310(4)	C(9)-C(10)	1.382(4)
C(9)-C(14)	1.390(4)	C(9)-N(1)	1.424(4)
C(10)-C(11)	1.383(5)	C(10)-N(5)	1.474(4)
C(11)-C(12)	1.378(4)	C(12)-C(13)	1.385(4)
C(12)-N(6)	1.467(5)	C(13)-C(14)	1.361(5)
C(14)-N(7)	1.492(4)	N(3)-O(1)	1.222(5)
N(3)-O(2)	1.217(4)	N(4)-O(3)	1.226(4)
N(4)-O(4)	1.226(4)	N(5)-O(5)	1.219(4)
N(5)-O(6)	1.195(4)	N(6)-O(7)	1.226(4)
N(6)-O(8)	1.223(4)	N(7)-O(9)	1.209(4)
N(7)-O(10)	1.193(5)		

Bond angle	Angle, deg	Bond angle	Angle, deg
C(2)-C(1)-C(6)	124.8(3)	C(2)-C(1)-N(1)	104.7(3)
C(6)-C(1)-N(1)	130.4(3)	C(1)-C(2)-C(3)	117.4(3)
C(1)-C(2)-N(2)	110.2(3)	C(3)-C(2)-N(2)	132.3(3)
C(2)-C(3)-C(4)	119.6(3)	C(2)-C(3)-N(4)	122.5(3)
C(4)-C(3)-N(4)	117.9(3)	C(3)-C(4)-C(5)	119.7(3)
C(4)-C(5)-C(6)	124.2(3)	C(4)-C(5)-N(3)	117.5(3)
C(6)-C(5)-N(3)	118.3(3)	C(1)-C(6)-C(5)	114.2(3)
C(8)-C(7)-N(1)	121.7(3)	C(8)-C(7)-N(2)	125.3(3)
N(1)-C(7)-N(2)	112.9(3)	C(10)-C(9)-C(14)	116.4(3)
C(10)-C(9)-N(1)	120.7(2)	C(14)-C(9)-N(1)	122.9(2)
C(9)-C(10)-C(11)	123.5(3)	C(9)-C(10)-N(5)	119.0(3)
C(11)-C(10)-N(5)	117.4(2)	C(10)-C(11)-C(12)	116.6(3)
C(11)-C(12)-C(13)	122.5(3)	C(11)-C(12)-N(6)	119.6(3)
C(13)-C(12)-N(6)	117.8(3)	C(12)-C(13)-C(14)	118.1(3)
C(9)-C(14)-C(13)	122.7(3)	C(9)-C(14)-N(7)	121.0(3)
C(13)-C(14)-N(7)	116.3(3)	C(1)-N(1)-C(7)	106.8(3)
C(1)-N(1)-C(9)	124.3(3)	C(7)-N(1)-C(9)	127.6(2)
C(2)-N(2)-C(7)	105.3(3)	C(5)-N(3)-O(1)	117.9(3)
C(5)-N(3)-O(2)	118.4(3)	O(1)-N(3)-O(2)	123.7(3)
C(3)-N(4)-O(3)	117.9(3)	C(3)-N(4)-O(4)	118.8(3)
O(3)-N(4)-O(4)	123.3(3)	C(10)-N(5)-O(5)	116.3(3)
C(10)-N(5)-O(6)	117.4(3)	O(5)-N(5)-O(6)	126.3(3)
C(12)-N(6)-O(7)	117.8(3)	C(12)-N(6)-O(8)	117.6(3)
O(7)-N(6)-O(8)	124.6(3)	C(14)-N(7)-O(9)	117.0(3)
C(14)-N(7)-O(10)	118.4(3)	O(9)-N(7)-O(10)	124.5(3)

TABLE 5. Bond Lengths, Å, and Bond Angles, deg, for **21b**, Form II.

Bond	Length, Å	Bond	Length, Å
C(1)-C(2)	1.403(5)	C(1)-C(6)	1.381(5)
C(1)-N(1)	1.387(5)	C(2)-C(3)	1.406(5)
C(2)-N(2)	1.374(5)	C(3)-C(4)	1.376(6)
C(3)-N(4)	1.452(5)	C(4)-C(5)	1.379(5)
C(5)-C(6)	1.378(5)	C(5)-N(3)	1.467(5)
C(7)-C(8)	1.484(6)	C(7)-N(1)	1.375(5)
C(7)-N(2)	1.310(4)	C(9)-C(10)	1.404(4)
C(9)-C(14)	1.385(5)	C(9)-N(1)	1.421(4)
C(10)-C(11)	1.379(5)	C(10)-N(5)	1.479(5)
C(11)-C(12)	1.368(5)	C(12)-C(13)	1.361(5)
C(12)-N(6)	1.473(5)	C(13)-C(14)	1.382(5)
C(14)-N(7)	1.470(4)	N(3)-O(1)	1.217(5)
N(3)-O(2)	1.223(5)	N(4)-O(3)	1.205(5)
N(4)-O(4)	1.187(7)	N(5)-O(5)	1.192(4)
N(5)-O(6)	1.209(5)	N(6)-O(7)	1.207(4)
N(6)-O(8)	1.209(5)	N(7)-O(9)	1.175(5)
N(7)-O(10)	1.180(5)		

Bond angle	Angle, deg	Bond angle	Angle, deg
C(2)-C(1)-C(6)	124.5(3)	C(2)-C(1)-N(1)	104.3(3)
C(6)-C(1)-N(1)	131.1(3)	C(1)-C(2)-C(3)	116.7(3)
C(1)-C(2)-N(2)	110.8(3)	C(3)-C(2)-N(2)	132.5(3)
C(2)-C(3)-C(4)	120.4(3)	C(2)-C(3)-N(4)	121.6(3)
C(4)-C(3)-N(4)	118.1(3)	C(3)-C(4)-C(5)	119.5(3)
C(4)-C(5)-C(6)	123.7(4)	C(4)-C(5)-N(3)	118.3(3)
C(6)-C(5)-N(3)	118.0(3)	C(1)-C(6)-C(5)	115.2(3)
C(8)-C(7)-N(1)	122.2(3)	C(8)-C(7)-N(2)	125.2(3)
N(1)-C(7)-N(2)	112.6(3)	C(10)-C(9)-C(14)	116.6(3)
C(10)-C(9)-N(1)	121.9(3)	C(14)-C(9)-N(1)	121.5(3)
C(9)-C(10)-C(11)	121.5(3)	C(9)-C(10)-N(5)	121.6(3)
C(11)-C(10)-N(5)	116.9(3)	C(10)-C(11)-C(12)	118.3(3)
C(11)-C(12)-C(13)	123.2(3)	C(11)-C(12)-N(6)	118.5(3)
C(13)-C(12)-N(6)	118.2(3)	C(12)-C(13)-C(14)	117.3(3)
C(9)-C(14)-C(13)	123.0(3)	C(9)-C(14)-N(7)	121.5(3)
C(13)-C(14)-N(7)	115.6(3)	C(1)-N(1)-C(7)	107.0(3)
C(1)-N(1)-C(9)	125.1(3)	C(7)-N(1)-C(9)	127.5(3)
C(2)-N(2)-C(7)	105.4(3)	C(5)-N(3)-O(1)	118.1(4)
C(5)-N(3)-O(2)	117.6(4)	O(1)-N(3)-O(2)	124.4(4)
C(3)-N(4)-O(3)	119.3(4)	C(3)-N(4)-O(4)	118.4(3)
O(3)-N(4)-O(4)	122.2(4)	C(10)-N(5)-O(5)	120.5(3)
C(10)-N(5)-O(6)	116.1(3)	O(5)-N(5)-O(6)	123.4(3)
C(12)-N(6)-O(7)	118.2(3)	C(12)-N(6)-O(8)	117.9(3)
O(7)-N(6)-O(8)	123.8(3)	C(14)-N(7)-O(9)	118.4(3)
C(14)-N(7)-O(10)	118.4(4)	O(9)-N(7)-O(10)	123.1(4)

The structures of forms I and II show no unusual or unexpected features. Furthermore, the two forms exhibit much similarity, while such differences as there are are relatively minor. These differences and similarities may be seen in Figure 3 in which the two structures are overlaid. In form I the benzimidazole system is planar; in form II the imidazole ring deviates from the plane of the aromatic ring, but only by an angle of 3.1 deg. The corresponding benzimidazole bond lengths and bond angles are essentially the same in the two forms and agree well with the expected parameters. The nitro group O(3)-N(4)-O(4) (i.e., that in the 4-position) deviates from the plane of the aromatic ring by only 2.7 and 2.6 deg; the O(1)-N(3)-O(2) group (at the 6-position) deviates by 11.7 and 12.2 deg, in order to relieve steric crowding by the nearby picryl group. As expected, the picryl group is far from the plane of the benzimidazole. In form I the plane of the picryl group is 72.9 deg from that of the benzimidazole system; in form II the angle between the planes is 87.7 deg. On the other hand the N(1)-C(9) bond is further from the plane of the benzimidazole in form I; in other words N(1) is more pyramidal in form I and more trigonal in form II. Apparently, there is also some minor variation in bond lengths in the picryl ring in forms I and II; however, this may well be attributable to the fact that C(12) was refined anisotropically in form I. Finally, there is also some variation in the angle of rotation of the nitro groups in the two forms (Table 6) and in the C-N and N-O bond lengths. As was found in earlier work (Reference 9), no apparent correlation between the bond lengths and the angle of rotation of the nitro-groups exists.

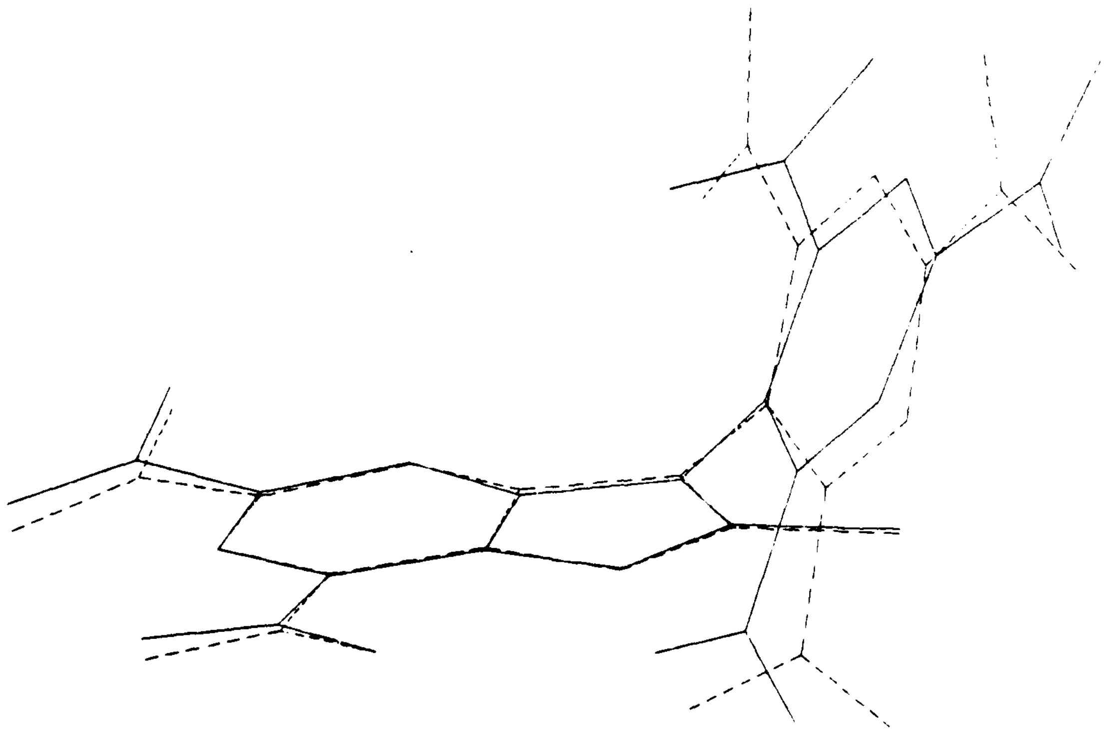


FIGURE 3. Comparison of the Two Forms of 21b. Solid line is Form I; dotted line is form II.

TABLE 6. Conformational Differences Between Form I (Tabular) and Form II (Rods) of **21b**.

Angle	Form I, tabular, deg	Form II, rod, deg
O(1)-N(3)-O(2) Rotation	11.7	12.2
O(3)-N(4)-O(4) Rotation	2.7	2.6
Picryl ring rotation to benzimidazole plane	72.9	87.7
O(5)-N(5)-O(6) Rotation	63.5	12.6
O(7)-N(6)-O(8) Rotation	8.8	18.2
O(9)-N(7)-O(10) Rotation	26.5	28.7

The packing plots for forms I and II of **21b** are shown in Figures 4 and 5. However neither these plots nor the short intermolecular van der Waals -O...H- contacts fully explains the nitro-group rotation, picryl-group orientation, or consequent density variation between the two forms. Potential energy minimization calculations might clarify the important factors.

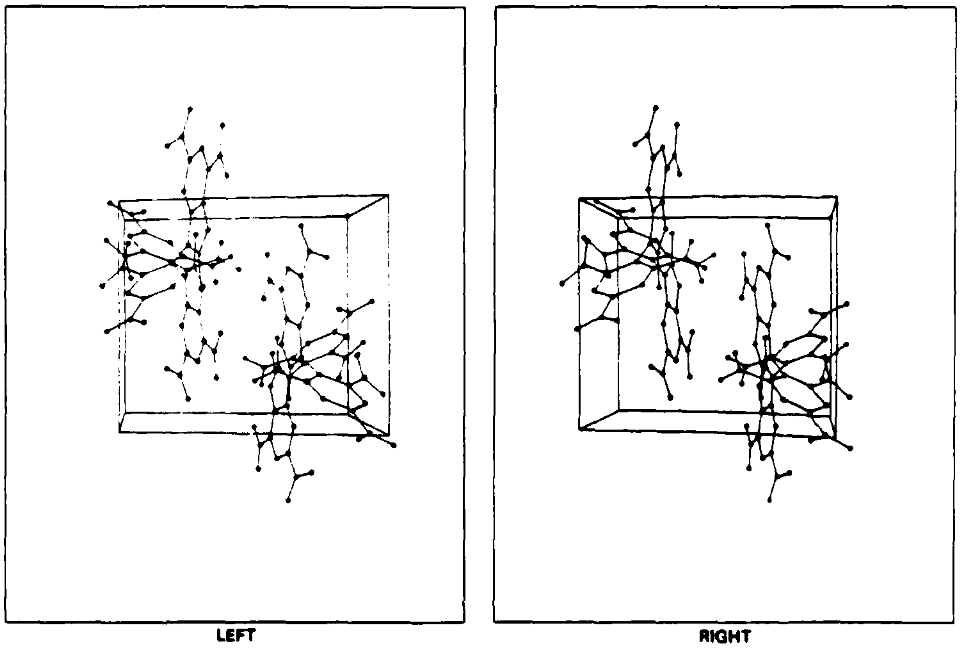


FIGURE 4. Stereo Packing Plot of Tabular Crystals, Form I of **21b**.

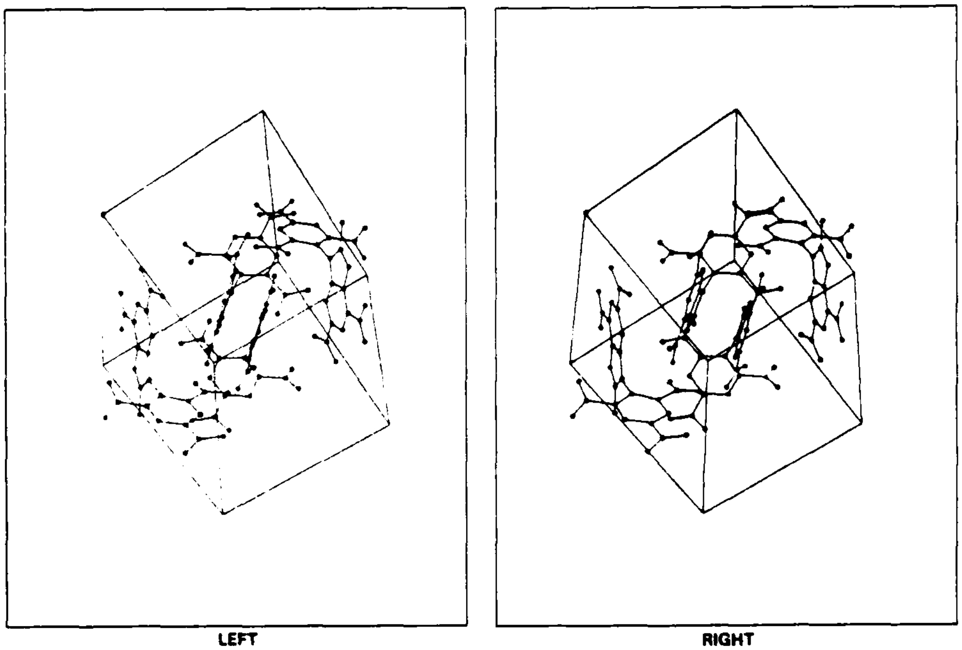
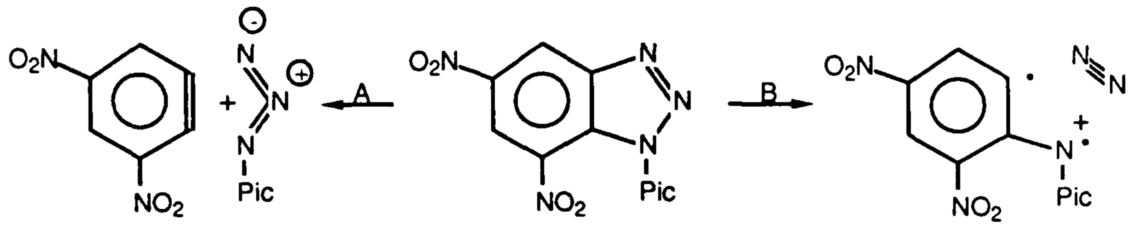


FIGURE 5. Stereo Packing Plot of Rod Crystals, Form II of **21b**.

The impact sensitivity of 1-picryl-4,6-dinitrobenzimidazole (**21a**) was measured using the Bureau of Mines machine with the 2.5 kg drop weight and was found to be 91 cm. This is about three times the drop height for the picrylbenzotriazoles and confirms the hypothesis that the Pic-N-N=N moiety contains the trigger-linkage for impact initiation of these explosives. It is interesting to note that the impact sensitivity of picryl azide is about 8 cm, and some speculation regarding the initial reaction during impact initiation seems warranted. One possibility is initial cleavage of the triazole to give picryl azide and a dinitrobenzyne equivalent (Pathway A). Further decomposition of these species would afford propagation of the explosive reaction. This pathway would not be available to the picrylbenzimidazoles and may account for their greater stability. An alternative explanation might be cleavage of the triazole with the elimination of nitrogen to leave a diradical species which would propagate further reaction (Pathway B). Once again this mode of decomposition would not be available to the picrylbenzimidazoles, since hydrogen cyanide would not be such a favorable leaving species. Further, the picryl group would ease such an elimination and would certainly stabilize the resultant radical species. Such stabilization may also explain the steady increase in the impact sensitivity of the benzotriazoles with increasing nitro-substitution on the pendant phenyl ring (Reference 1). (It might be hoped that some clue to the nature of the initial reaction might be gained by analogy with the mass spectra of the benzotriazoles and benzimidazoles. Unfortunately, however, no evidence for either nitrogen or picryl azide elimination could be discerned under electron impact. While the parent ion was detected in each case, albeit at a relatively low intensity, massive fragmentation was evident and the most prominent peaks were all at low mass numbers).



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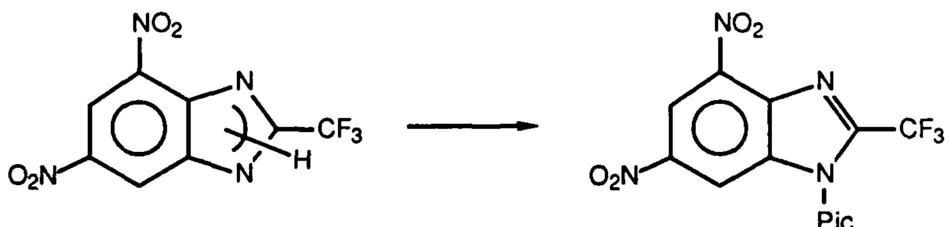
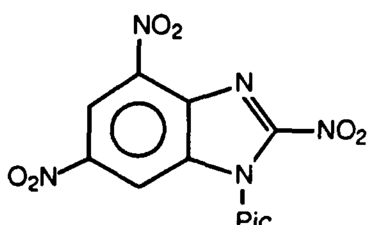
These results are quite satisfying in that they confirm our initial hypothesis regarding the initiation of the benzotriazoles on impact, and they give some indications of the initial reaction during the initiation process. However, the benzimidazoles prepared in this study show quite unexceptional explosive properties. They are quite insensitive to impact initiation, and **21a** and **b** appear to be thermally stable below 330 and 280°C, respectively. On the other hand, the densities are rather low, as might be expected with the benzimidazole and picryl moieties being almost orthogonal. The tabular and rod forms of the methyl derivative (**21b**) have densities of 1.658 and 1.712, respectively, compared with a calculated value of 1.704 (Reference 3); the density of **21a** was measured by gas pycnometry as 1.708, compared with a calculated density of 1.738 (Reference 3). (This latter apparent discrepancy may be due to the small and ill-defined crystalline form of **21a**, and the actual crystal density may be higher.) Furthermore **21a** and **21b** are predicted to have the uninspiring detonation velocities of 6937 and 6655 m/s and detonation pressures of 191 and 165 kbar respectively (Reference 4). The question then arises, how can the explosive properties of these benzimidazoles be enhanced? Substitution with the trifluoromethyl group in **21c** would increase the density and the oxygen balance, thereby improving the detonation parameters. The potential precursor (**19c**) has been prepared, but coupling with picryl fluoride was unsuccessful. Further nitration as in **22** should also increase oxygen balance, but a suitable reaction pathway has not been devised. Substitution with a second picryl group as in **23** is a possibility but, while thermal stability might be further enhanced, improvement of detonation parameters is likely to be minimal.



19c **21c**



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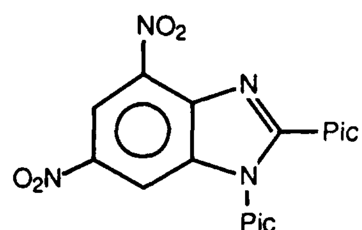

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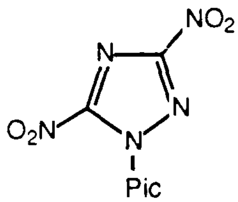
If, however, this result may be extrapolated into different ring systems, it may provide a strategem for designing powerful but insensitive heterocyclic explosives, simply by avoiding the Pic-N-N=N functionality. There appears to be some support for this suggestion in the work of Neuman, who prepared several isomeric pairs of 1- and 2-picryl-1,2,3-triazoles, and found in each case that the 1-picryl isomer was sensitive to impact initiation while the 2-picryl isomer was insensitive (Reference 10). This result has been rationalized by invoking a mechanism similar to Pathway B to account for the initiation of the 1-picryl-1,2,3-triazoles (Reference 11). A logical extension of this work is then the synthesis and evaluation of such materials as 1-picryl-3,5-dinitro-1,2,4-triazole (**24**) and 1-picryl-2,4,5-trinitroimidazole (**25**), which will be the subject of a future report.



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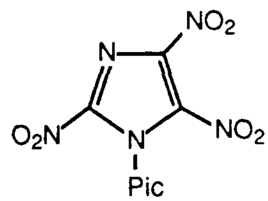

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EXPERIMENTAL SECTION

Melting points were determined in capillary tubes using a Buchi 510 melting point apparatus. More detailed thermal behavior was determined using a DuPont 1090 Thermal Analyzer. Infrared spectra were determined in KBr disks using a Perkin-Elmer Model 1330 spectrophotometer. ^{1}H-NMR spectra were determined in d_6-acetone solutions (unless otherwise stated) using an IBM NR-80 instrument; ^{13}C-NMR spectra were recorded on the same instrument operating at 20 Hz or on a Nicolet NT-200 instrument operating at 50 Hz. Mass spectra were determined using a Perkin-Elmer 5985 gas chromatograph/mass spectrometer (GC/MS). **WARNING: Many of the compounds described in this report are explosives which may be subject to accidental initiation by such stimuli as friction, heat and impact. Therefore, appropriate precautions should be taken in their handling and/or use.**

2-AMINO-4,6-DINITRODIPHENYLAMINE (1)

2,4,6-Trinitrodiphenylamine (8.00 g, 26.3 mmol; prepared by condensation of aniline with picryl chloride (Reference 12)) was dissolved in glacial acetic acid (400 mL), and was stirred mechanically at ambient temperature under an atmosphere of dry nitrogen. Iron powder (100 mesh, 4 x 1.20 g, 85.7 mmol) was added at 30 min intervals (References 1 and 13). The reaction was allowed to continue at ambient temperature; after a total reaction time of 3 h, the mixture was filtered, and the filtrate was quenched in ice/water. Filtration gave **1** as a brick-red solid (6.3 g, 70%), recrystallized from ethanol as red plates, mp 160 to 161°C. IR: 3490, 3390, 3350, 1590, 1550, 1530, 1500, 1350, 1330, 1300, 1270, 770, 760, 750, 700 cm^{-1}; ^{1}H-NMR: δ 8.11 (d, J = 2.62 Hz, ^{1}H, H_5), 8.06 (br s, 1 H, NH), 7.92 (d, J = 2.62 Hz, 1 H, H_3), 7.60 to 6.60 (m, 5 H, C_6H_5), 5.36 (br s, 2 H, NH_2).

1-(2',4',6'-TRINITROPHENYL)BENZIMIDAZOLE (9)

o-Phenylenediamine (1.50 g, 13.9 mmol) and picryl chloride (2.50 g, 10.1 mmol) were dissolved in methanol (50 mL) and stirred at ambient temperature overnight. The solution turned dark, and a mixture of red and yellow crystals were precipitated. The crystals were filtered off and thoroughly washed with water (50 mL) to give a uniform brick-red solid, identified as the required *N*-picryl-*o*-phenylenediamine (2.85 g, 89%), which was recrystallized from xylene as red needles, mp 181°C. IR: 3430, 3360, 3280, 3110, 1630, 1590, 1560, 1530, 1510, 1360, 1340, 1320, 1300, 1180, 760, 740, 730 cm^{-1}; ^{1}H-NMR: δ 9.01 (s, 2 H), 7.20 to 6.40 (m, 4 H), 3.05 (br s, 3 H, NH's). *N*-Picryl-*o*-phenylenediamine (1.40 g, 4.4 mmol) was warmed in trimethylorthoformate (20 mL) for 1 h. Evaporation to dryness and recrystallization from chloroform gave a yellow powder (0.95 g, 66%), identified as **9**, mp 211 to 213°C. IR: 1610, 1560, 1500, 1350, 1340, 1300, 1240, 1150, 920, 780, 760 cm^{-1}; ^{1}H-NMR: δ 9.39 (s, 2H), 8.35 (s, 1 H), 7.91 to 7.68 (m, 1 H), 7.54 to 7.08 (m, 3 H); m/z: 329 (parent ion), 255, 225, 213, 191, 164.

1-PHENYL-5,7-DINITROBENZIMIDAZOLE (11a)

Pathway A. 2-Amino-4,6-dinitro-diphenylamine (**1**) (1.00 g, 3.7 mmol) was dissolved in trimethylorthoformate (10 mL). Ninety-six percent sulfuric acid (1 drop) was added, and the solution was heated under reflux for 2 h. A grey-tan solid precipitated, which was filtered off and recrystallized from ethanol as pale yellow platelets (0.88 g, 85%), identified as **11a**, mp 218°C.

Pathway B. 2-Amino-4,6-dinitrodiphenylamine (**1**) (1.64 g, 6.0 mmol) was dissolved in 97% formic acid (10 mL) and heated under reflux for 1 h. The reaction mixture was quenched on ice/water (300 mL), filtered, and recrystallized from ethanol as pale yellow platelets (1.54 g, 91%) identified as **11a**, mp 218°C. IR: 3120, 3040, 1620, 1600, 1590, 1530, 1500, 1465, 1350, 1340, 1290, 1230, 1220, 1190, 950, 930, 810, 740, 700 cm^{-1}; ^{1}H-NMR: δ 9.87 (d, J = 2.10 Hz, 1 H, H_6), 8.83 (d, H = 2.10 Hz, 1 H, H_4), 8.68 (s, 1 H, H_2), 7.58 (s, 5 H, C_6H_5); m/z: 284 (parent ion and base peak), 267, 239, 221, 192, 164, 77, 51.

1-PHENYL-2-METHYL-5,7-DINITROBENZIMIDAZOLE (11b)

2-Amino-4,6-dinitrodiphenylamine (**1**) (1.00 g, 3.7 mmol) was dissolved in glacial acetic acid (7 mL) and acetic anhydride (5 mL), and the reaction mixture was heated under reflux overnight. The reaction mixture was cooled and quenched on ice/water (400 mL) to give a grey solid (1.08 g, 99%) identified as **11b** and recrystallized from ethanol as off-white needles (0.80 g, 74%), mp 189°C. IR: 3100, 3040, 1630, 1600, 1530, 1500, 1470, 1390, 1370, 1350, 1300, 1220, 820, 760, 710 cm^{-1}; ^{1}H-NMR: δ 8.78 (d, J = 2.10 Hz, 1 H, H_6), 8.67 (d, J = 2.10 Hz, 1 H, H_4), 7.59 (m, 5 H, C_6H_5), 2.48 (s, 3 H, CH_3); m/z: 298 (parent ion and base peak), 281, 253, 222, 235, 205, 164, 77, 51.

2-(TRIFLUOROACETAMIDO)-4,6-DINITRODIPHENYLAMINE (10c)

2-Amino-4,6-diphenylamine (**1**) (0.50 g, 1.8 mmol) was added to trifluoroacetic anhydride (5 mL), and the mixture was stirred under reflux for 3 h. The amine disappeared, and an orange solid precipitated. Work up by quenching in water, or by evaporation of the solvent, gave a quantitative yield (0.675 g) of **10c** as an orange powder recrystallized from dichloromethane/hexane as orange crystals, mp 142°C. IR: 3350, 1760, 1620, 1600, 1550, 1530, 1500, 1460, 1340, 1280, 1250, 1200, 1180, 1150, 1090, 940, 920, 900, 825, 760, 740, 730, 700 cm^{-1}; ^{1}H-NMR: δ 9.75 (br s, 1 H, NH), 9.32 (br s, 1 H, NH), 8.92 (d, J = 2.71 Hz, 1 H, H_5), 8.61 (d, J = 2.71 Hz, 1 H, H_3), 7.00 to 7.50 (m, 5 H, C_6H_5); m/z: 370 (parent ion and base peak), 301, 181, 179, 154, 77, 69, 51.

1-PHENYL-2-TRIFLUOROMETHYL-5,7-DINITROBENZIMIDAZOLE (11c)

2-(Trifluoroacetamido)-4,6-dinitrodiphenylamine (**10c**) (0.73 g, 2.0 mmol) was dissolved in 96% sulfuric acid (25 mL) and stirred at ambient temperature overnight. Quenching on ice/water (200 mL) gave **11c** as an off-white solid (0.53 g, 67%), which was recrystallized from ethanol as off-white needles, mp 114°C. IR: 1600, 1550, 1530, 1500, 1400, 1350, 1260, 1220, 1200, 1170, 1150, 820, 760, 740, 730, 700 cm^{-1}; ^{1}H-NMR: δ 9.12 (d, J = 2.08 Hz, 1 H, H_6), 8.89 (d, J = 2.08 Hz, 1 H, H_4), 7.66 (s, 5 H, C_6H_5); m/z: 352 (parent ion and base peak), 335, 307, 261, 165, 164, 138, 77, 69, 51.

NITRATION)F 1-(2',4',6'-TRINITROPHENYL)BENZIMIDAZOLE (9)

1-(2',4',6'-Trinitrophenyl)benzimidazole (**9**) (2.50 g, 7.6 mmol) was dissolved in a mixture of 96% sulfuric acid (20 mL) and 100% nitric acid (20 mL), and heated under reflux overnight. The reaction mixture was quenched in ice/water (200 mL) to give a white solid (2.60 g, 82%). The crude reaction product was identified by IR and NMR as 1-(2',4',6'-trinitrophenyl)-5,6-dinitrobenzimidazole (**14a**) (*vide infra*), but attempted recrystallization from ethanol resulted in hydrolysis to 2-(2',4',6'-trinitrophenylamino)-4,5-dinitroaniline (**15**) as an electrostatically charged yellow solid (1.28 g, 39%), mp 275°C (dec). IR: 3490, 3380, 3250, 1650, 1640, 1600, 1350, 1320, 1300, 1260 cm^{-1}; ^{1}H-NMR: δ 9.09 (s, 2 H, $H_{3,5}$), 8.00 (s, 1 H, H_2), 7.26 (s, 1 H, H_6).

1-(2',4',6'-TRINITROPHENYL)-5,6-DINITROBENZIMIDAZOLE (14a)

2-(2',4',6'-Trinitrophenylamino)-4,5-dinitroaniline (**15**) (0.75 g, 1.8 mmol) was dissolved in trimethylorthoformate (20 mL) and heated under reflux for 2 h. Evaporation to dryness gave a quantitative yield (0.77 g) of tan solid, identified as **14a** and recrystallized from ethanol/acetone as pale yellow crystals (0.52 g, 68%), mp 242 to 245°C (dec). ^{1}H-NMR showed that the product was contaminated with a small amount (less than 5%) of the amine (**15**), which could not be removed either by flash chromatography or by repeated recrystallization. IR: 3100, 1620, 1550, 1500, 1380, 1350, 1310, 915, 730 cm^{-1}; ^{1}H-NMR: δ 9.50 (s, 2 H, $H_{3',5'}$), 8.89 (s, 1 H, H_2), 8.64 (s, 1 H, H_7), 8.39 (s, 1 H, H_4); m/z: 419 (parent ion), 345, and smaller peaks.

2-METHYL-1-(2',4',6'-TRINITROPHENYL)-5,6-DINITROBENZIMIDAZOLE (14b)

2-(2',4',6'-Trinitrophenylamino)-4,5-dinitroaniline (**15**) (0.28 g, 0.7 mmol) was added to glacial acetic acid (3 mL) and acetic anhydride (4 mL) and heated under reflux for 3 h. The reaction solution was cooled and quenched in ice/water (50 mL) and filtered to give a pale tan solid (0.24 g, 81%) identified as **14b**. Recrystallization from ethanol gave a pale yellow solid (0.12 g), mp 269 to 273°C (dec). IR: 3000, 1610, 1500, 1480, 1350, 1300, 1250, 1090, 920, 890, 850, 830, 720 cm^{-1}; ^{1}H-NMR: 9.54 (s, 2 H, $H_{3',5'}$), 8.46 (s, 1 H, H_7), 8.22 (s, 1 H, H_4), 2.61 (s, 3 H, CH_3); m/z: 433 (parent ion), 388, and smaller peaks.

4,6(5,7)-DINITROBENZIMIDAZOLE (19a)

3,5-Dinitro-1,2-diamino-benzene (**17**) (Reference 8) (1.00 g, 5.0 mmol) was dissolved in 96% formic acid (20 mL), and heated under reflux for 3 h. The solution was cooled and quenched in ice/water (300 mL) to give a tan solid (0.92 g, 88%),, identified as **19a**. Recrystallization from methanol gave fluffy pale tan crystals (0.81 g), mp 246°C. IR: 3300, 3100, 3020, 1630, 1590, 1520, 1480, 1470, 1340, 1290, 1090, 1080, 940, 810, 740, 620 cm^{-1}; ^{1}H-NMR: (a) d_6-acetone: see Table 2; (b) d_6-DMSO: δ 8.95 (d, J = 2.03 Hz, 1 H, H_5), 8.82 (d, J = 2.03 Hz, 1 H, H_7), 8.74 (s, 1 H, H_2); m/z: 208 (parent ion and base peak), 178, 162, 132, 116, 115, 89, 62.

2-METHYL-4,6(5,7)-DINITROBENZIMIDAZOLE (19b)

3,5-Dinitro-1,2-diaminobenzene (**17**) (Reference 8) (1.00 g, 5.0 mmol) was suspended in glacial acetic acid (10 mL) and acetic anhydride (10 mL) and heated under reflux for 4 h. The solution was cooled and quenched in ice/water (120 mL) to give an off-white solid (0.95 g, 85%) identified as **19b**. Recrystallization from ethanol gave tan needles (0.81 g), mp 248 to 252°C (dec). IR: 3360, 3100, 3040, 1680, 1590, 1530, 1470, 1390, 1350, 1300, 1190, 940, 820, 740, 640 cm^{-1};

^{1}H-NMR: (a) d_6-acetone: see Table 2; (b) d_6-DMSO: 8.74 (s, 2 H, $H_{5,7}$), 2.64 (s, 3 H, CH_3); m/z: 222 (parent ion and base peak), 176, 130, 129.

2-TRIFLUOROMETHYL-4,6(5,7)-DINITROBENZIMIDAZOLE (19c)

3,5-Dinitro-1,2-diaminobenzene (**17**) (Reference 8) (1.00 g, 5.0 mmol) was suspended in trifluoroacetic anhydride (15 mL) and stirred at ambient temperature for 3 h with the formation of a yellow solid. Evaporation to dryness gave a yellow solid (1.05 g, 71%), which was recrystallized from ethanol to give 2-trifluoroacetamido-3,5-dinitroaniline (0.75 g) as yellow crystals, mp 166 to 169°C. IR: 3460, 3340, 3260, 1740, 1630, 1590, 1540, 1520, 1340, 1280, 1250, 1210, 1160, 900, 740, 550 cm^{-1}; ^{1}H-NMR: δ 8.97 (d, J = 2.68 Hz, 1 H, H_4), 8.42 (d, J = 2.68 Hz, 1 H, H_6); m/z: 294 (parent ion), 276, 225 (base peak), 179, 133, 78, 69. The amide (0.45 g, 1.5 mmol) was dissolved in 96% formic acid (15 mL) and heated under reflux for 4 h. The solution was quenched in ice/water (50 mL) and extracted with dichloromethane (4 x 100 mL) to give an off-white solid (0.41 g; 97%) identified as **19c**, which was recrystallized from benzene as white needles, mp 154 to 156°C. IR: 3300, 1600, 1570, 1550, 1480, 1360, 1350, 1310, 1250, 1200, 1190, 1160, 1130, 1070, 900, 810, 750, 730, 690 cm^{-1}; ^{1}H-NMR: δ 9.11 (s); m/z: 276 (parent ion and base peak), 257, 246, 230, 200, 183, 183, 113, 69, 62.

1-METHYL-4,6-DINITROBENZIMIDAZOLE (20a)

4,6(5,7)-Dinitrobenzimidazole (**19a**) (0.40 g, 1.9 mmol) was added to a suspension of sodium hydride (0.16 g, 6.7 mmol) in dry dioxane (40 mL) and stirred at ambient temperature for 30 min. Methyl iodide (8 mL) was added, and the solution was heated under reflux overnight. Evaporation to dryness left a residue (0.50 g), which was recrystallized from methanol to yield **20a** as tan needles (0.22 g, 52%), mp 195 to 197°C. IR: 3100, 1590, 1530, 1380, 1340, 1270, 1070, 930, 800, 750, 690, 620 cm^{-1}; ^{1}H-NMR: see Table 2; m/z: 222 (parent ion and base peak), 192, 146, 130, 129, 118, 91, 88, 76, 62.

1,2-DIMETHYL-4,6-DINITROBENZIMIDAZOLE (20b)

2-Methyl-4,6(5,7)-dinitrobenzimidazole (**19b**) (0.40 g, 1 8 mmol) was added to a suspension of sodium hydride (0.20 g, 8.7 mmol) in dry dioxane (40 mL) and stirred at ambient temperature for 30 min. Methyl iodide (10 mL) was added, and the solution was gently warmed to reflux for 3 h. Evaporation to dryness and extraction with dichloromethane gave a residue, shown by NMR to be a mixture (ca. 1:1) of product and starting material. Flash chromatography (ethyl acetate/silica) yielded starting material (**19b**, 0.20 g) and the desired product (**20b**, 0.18 g, 42%), recrystallized from methanol as a fluffy white solid (0.12 g), mp 217 to 220°C. IR: 3100, 1590, 1520, 1450, 1370, 1360, 1350, 1250, 1070, 930, 890, 830, 740, 730, 720 cm^{-1}; ^{1}H-NMR: d_6-acetone: see Table 2; d_6-DMSO: δ 8.93 (d, J = 2.10 Hz, 1 H, H_5), 8.72 (d, J = 2.10 Hz, 1 H, H_7), 3.93 (s, 3 H, N-CH_3), 2.69 (s, 3 H, C-CH_3); m/z: 236 (parent ion and base peak), 206, 144, 143, 117, 91, 69, 57, 55, 43.

1-(2',4',6'-TRINITROPHENYL)-4,6-DINITROBENZIMIDAZOLE (21a)

Pathway A. 4,6(5,7)-Dinitrobenzimidazole (**19a**) (0.40 g, 1.9 mmol) and 1-fluoro-2,4,6-trinitrobenzene (Reference 14) (0.80 g, 3.5 mmol) were dissolved in dimethylformamide (12 mL), and the solution was stirred at ambient temperature for 36 h. The reaction solution was quenched in water (160 mL) and then filtered to yield a yellow solid (0.76 g,94%) identified as **21a**. Recrystallization from acetone gave a pale yellow electrostatically charged solid, mp 330°C (dec).

Pathway B. 4,6(5,7)-Dinitrobenzimidazole (**19a**) (0.10 g, 0.5 mmol) and 1-fluoro-2,4,6-trinitrobenzene (Reference 14) (0.20 g, 0.8 mmol) were dissolved in DMSO (2 mL), and triethylamine (10 drops) was added. The solution immediately turned dark. The reaction solution was stirred at ambient temperature for 2 h and then quenched in water (25 mL). Filtration gave a red-brown solid, which was recrystallized from acetone/ethanol to give **21a** as a pale tan solid (0.10 g, 50%).

Pathway C. 4,6(5,7)-Dinitrobenzimidazole (**19a**) (0.10 g, 0.5 mmol) was added to a suspension of sodium hydride (0.04 g, 1.7 mmol) in dry dioxane (3 mL) and stirred at ambient temperature for 30 min. 1-Fluoro-2,4,6-trinitrobenzene (0.20 g, 0.8 mmol) was added, and the solution was warmed to 50°C for 8 h. Evaporation to dryness and recrystallization from acetone gave **21a** as a pale yellow solid (0.05 g, 25%). IR: 3100, 1610, 1550, 1490, 1370, 1340, 1300, 1250, 940, 810, 720 cm^{-1}; ^{1}H-NMR: see Table 2; m/z: 419 (parent ion), 345, 315, 303, 269, 208, 104, 88, 74 (base peak), 62.

2-METHYL-1-(2',4',6'-TRINITROPHENYL)-4,6-DINITROBENZIMIDAZOLE (21b)

2-Methyl-4,6(5,7)-dinitrobenzimidazole (**19b**) (0.40 g, 1.8 mmol) and 1-fluoro-2,4,6-trinitrobenzene (Reference 14) (0.80 g, 3.5 mmol) were dissolved in dimethylformamide (5 mL) and stirred at ambient temperature for 24 h. The reaction solution was quenched in ice/water and filtered to give a tan solid (0.91 g, wet). Recrystallization from acetone/ethanol gave **21b** (0.63 g; 81%) as a mixture of orange-brown triangular platelets and cream-yellow rods, mp 290°C (dec). All spectroscopic evidence indicated that the two crystalline forms were composed of the same molecular species. IR: 3100, 3000, 1610, 1540, 1490, 1440, 1350, 1330, 1310, 1250, 1080, 940, 900, 830, 760, 740, 720, 680 cm^{-1}; ^{1}H-NMR: see Table 2; m/z: 433 (parent ion), 391, 340, 269, 222, 88, 74, 62, 43 (base peak).

SINGLE CRYSTAL X-RAY STRUCTURE OF TWO CRYSTALLINE FORMS OF 2-METHYL-1-(2',4',6'-TRINITROPHENYL)-4,6-DINITROBENZIMIDAZOLE (22b)

Unit cell and other crystallographic data are listed in Table 7. A flaw-free, orange-brown colored, triangular shaped tabular platelet of form I with dimensions 0.28 x 0.30 x 0.11 mm was selected for data collection. A flaw-free, cream-yellow colored six-sided rod of form II with dimensions 0.10 x 0.20 x 0.42 mm was selected for data collection. Unit cell dimensions were obtained by a constrained least-squares fit of 25 (form I) or 24 (form II) computer-centered reflections on a Nicolet R3 with monochromated Mo K_α radiation. Intensity data for both forms were collected in a similar manner, using $2\theta/\theta$ scans on a Nicolet R3 with monochromated Mo K_α. Data collection parameters were as follows: variable scan speed of 2 to 6deg/min; scan range of 1 deg < $K_{\alpha 1}$ to 1 deg > $K_{\alpha 2}$; 2θ range of 4 to 50 deg (to 46 deg for form II); h/-14 to 14/, k/0 to 12/, ℓ/-20 to 20/ for form I; h/-13 to 13 (partial + hkℓ octant)/, k/0 to 13/, ℓ/-15 to 15/ for form II; 3 check reflections every 93 reflections; check reflections (020), (01$\bar{6}$), ($\bar{5}$33) for form I; check reflections (600), (023), ($\bar{4}$31) for form II. The check reflections for form I exhibited a slight (< 5%) increase with time. Systematic absences observed in the diffractometer data of h0ℓ, ℓ = 2n + 1, 00ℓ, ℓ = 2n + 1, 0k0, k = 2n + 1, for form I and h0ℓ, h = 2n + 1, h00, h = 2n + 1, 0k0, k = 2n + 1 for form II uniquely defined the space groups as $P2_1/c$ for form I and $P2_1/a$ for form II. The intensity data were corrected for Lorentz and polarization effects but not for absorption.

TABLE 7. Crystallographic Data for **21b**, Form I and Form II, $C_{14}H_7N_7O_{10}$, M = 433.25.

Form I	Form II
Monoclinic $P2_1/c$	Monoclinic $P2_1/a$
a = 11.261(2)	a = 10.963(2)
b = 9.770(2)	b = 11.797(3)
c = 16.420(3) Å	c = 13.238(3) Å
β = 106.04(2) deg	β = 100.80(2) deg
V = 1736.3(6) $Å^3$	V = 1681.7(6) $Å^3$
z = 4	z = 4
D_x = 1.658 g/cm^3	D_x = 1.712 g/cm^3
λ (Mo K_α) = 0.71069 Å	λ (Mo K_α) = 0.71069 Å
μ = 1.35 cm^{-1}	μ = 1.35 cm^{-1}
F(000) = 800	F(000) = 800
T = 291 K	T = 291 K
R = 0.060	R = 0.059
For 2241 reflections with $\lvert F_o \rvert > 4\sigma(F)$	For 1838 reflections with $\lvert F_o \rvert > 3\sigma(F)$

Phasing for both structures was obtained with the multi-solution direct methods of SHELXTL (Reference 15). After the initial least-squares refinement, the hydrogen atoms were observed on difference Fourier maps. Subsequently the hydrogen atoms were included in both refinements with unconstrained thermal parameters, but geometrically constrained to be "riding" on their adjacent carbon atoms with fixed bond lengths of 0.96 Å. Refinement was by minimization of the function $[\Sigma w(|F_o|-k|F_c|)^2]$ using SHELXTL's blocked-cascade least-squares algorithm with $w = 1/[\sigma^2(F) + gF^2]$ (g = 0.00045 for form I, g = 0.0006 for form II). Refinement of both structures included anisotropic nitrogen, oxygen atoms and isotropic carboon, hydrogen atoms (except for C(7), C(8), and C(12) of form I which were refined anisotropically). Maximum shift to estimated standard deviation (esd) ratios were less than 0.04 during the last cycles. The final difference Fourier maps had peaks and troughs of +0.32 to -0.33 $e^-/Å^3$ for form I and +0.48 to -0.33 $e^-/Å^3$ for form II. The oxygen atoms and the hydrogen atoms of the methyl group in form II have relatively large thermal parameters. Final atomic coordinates and thermal parameters for form I and form II are listed in Tables 8 and 9 respectively. Other crystallographic data are to be found in Tables 10 through 13.

TABLE 8. Atom Coordinates, x 10^4, and Thermal Parameters, $Å^2$ x 10^3, for **21b**, Form I.

Atom	x	y	z	U_{iso}/U_{eq}
C(1)	2789(3)	5481(3)	5916(2)	29(1)
C(2)	3230(3)	5169(3)	5220(2)	32(1)
C(3)	3412(3)	3791(3)	5066(2)	36(1)
C(4)	3189(3)	2804(3)	5609(2)	37(1)
C(5)	2740(3)	3186(3)	6277(2)	36(1)
C(6)	2522(3)	4519(3)	6465(2)	34(1)
C(7)	3060(3)	7355(3)	5227(2)	37(1)[a]
C(8)	3119(4)	8845(3)	5038(3)	59(2)[a]
C(9)	2069(3)	7659(3)	6408(2)	29(1)
C(10)	2642(3)	7934(3)	7251(2)	30(1)
C(11)	2090(3)	8665(3)	7769(2)	35(1)
C(12)	934(3)	9193(3)	7394(2)	38(1)[a]
C(13)	308(3)	8943(3)	6554(2)	40(1)
C(14)	875(3)	8157(3)	6088(2)	36(1)
N(1)	2691(2)	6902(2)	5908(2)	31(1)[a]
N(2)	3400(3)	6360(3)	4806(2)	39(1)[a]
N(3)	2462(3)	2099(3)	6807(2)	45(1)[a]
N(4)	3803(3)	3335(3)	4336(2)	49(1)[a]
N(5)	3920(3)	7461(3)	7622(2)	45(1)[a]
N(6)	358(3)	10119(3)	7876(2)	50(1)[a]
N(7)	149(3)	7868(3)	5197(2)	50(1)[a]
O(1)	1875(3)	2402(3)	7305(2)	70(1)[a]
O(2)	2802(3)	940(2)	6716(2)	57(1)[a]
O(3)	3898(3)	2100(3)	4237(2)	81(1)[a]
O(4)	4038(2)	4196(3)	3860(2)	57(1)[a]
O(5)	4081(3)	6661(3)	8212(2)	81(1)[a]
O(6)	4699(2)	7918(4)	7332(2)	82(1)[a]
O(7)	892(3)	10302(3)	8626(2)	78(1)[a]
O(8)	-607(3)	10679(3)	7496(2)	67(1)[a]
O(9)	-663(3)	8668(3)	4871(2)	79(1)[a]
O(10)	383(3)	6841(4)	4870(2)	102(2)[a]

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE 9. Atom Coordinates, x 10^4, and Thermal Parameters, $Å^2$ x 10^3, for **21b**, Form II.

Atom	x	y	z	U_{iso}/U_{eq}
C(1)	1124(3)	7893(3)	2101(3)	36(1)
C(2)	437(3)	6929(3)	2263(3)	36(1)
C(3)	621(3)	5952(3)	1702(3)	39(1)
C(4)	1406(3)	5979(3)	1004(3)	43(1)
C(5)	2020(3)	6971(3)	865(3)	42(1)
C(6)	1913(3)	7955(3)	1403(3)	45(1)
C(7)	-122(3)	8218(3)	3212(3)	37(1)
C(8)	-754(4)	8855(3)	3933(3)	49(1)
C(9)	1302(3)	9801(3)	2925(3)	35(1)
C(10)	2335(3)	9983(3)	3712(3)	39(1)
C(11)	2911(4)	11025(3)	3854(3)	45(1)
(C12)	2425(3)	11900(3)	3227(3)	41(1)
C(13)	1391(3)	11796(3)	2483(3)	41(1)
C(14)	852(3)	10735(3)	2337(3)	37(1)
N(1)	752(3)	8712(2)	2731(2)	39(1)[a]
N(2)	-328(3)	7155(2)	2950(2)	40(1)[a]
N(3)	2807(3)	6991(4)	82(3)	55(1)[a]
N(4)	-15(3)	4896(3)	1826(3)	54(1)[a]
N(5)	2869(3)	9062(3)	4416(2)	53(1)[a]
N(6)	3069(3)	13001(3)	3344(3)	57(1)[a]
N(7)	-229(3)	10649(3)	1496(3)	57(1)[a]
O(1)	3495(3)	7799(3)	69(3)	80(1)[a]
O(2)	2725(3)	6193(3)	-516(2)	71(1)[a]
O(3)	121(3)	4097(2)	1291(2)	65(1)[a]
O(4)	-690(5)	4865(3)	2430(4)	145(3)[a]
O(5)	2318(3)	8194(2)	4443(3)	72(1)[a]
O(6)	3887(4)	9238(3)	4926(3)	114(2)[a]
O(7)	4129(3)	13028(3)	3804(3)	77(1)[a]
O(8)	2506(4)	13824(3)	2963(3)	101(2)[a]
O(9)	-827(4)	11467(3)	1257(3)	103(2)[a]
O(10)	-427(5)	9774(3)	1064(4)	149(2)[a]

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE 10. Anisotropic Thermal Parameters, Å^2 x 10^3, for **21b**, Form I.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(7)	51(2)	28(2)	35(2)	4(1)	16(2)	1(1)
C(8)	98(3)	30(2)	61(3)	11(2)	43(2)	10(2)
C(12)	50(2)	29(2)	46(2)	1(1)	30(2)	2(1)
N(1)	40(1)	27(1)	27(1)	1(1)	12(1)	2(1)
N(2)	60(2)	29(1)	33(1)	3(1)	21(1)	4(1)
N(3)	52(2)	40(2)	43(2)	7(1)	12(1)	-9(1)
N(4)	68(2)	38(2)	44(2)	-4(1)	22(2)	6(1)
N(5)	42(2)	55(2)	35(1)	-7(1)	6(1)	7(1)
N(6)	63(2)	39(2)	59(2)	1(1)	39(2)	5(1)
N(7)	44(2)	57(2)	42(2)	-5(1)	1(1)	-2(1)
O(1)	93(2)	55(2)	75(2)	14(1)	47(2)	-5(2)
O(2)	73(2)	30(1)	68(2)	13(1)	20(1)	-4(1)
O(3)	140(3)	35(1)	89(2)	-15(1)	65(2)	7(2)
O(4)	81(2)	51(2)	48(1)	2(1)	33(1)	12(1)
O(5)	73(2)	93(2)	70(2)	37(2)	8(2)	31(2)
O(6)	40(2)	134(3)	73(2)	12(2)	17(1)	3(2)
O(7)	104(2)	83(2)	56(2)	-11(2)	40(2)	29(2)
O(8)	61(2)	64(2)	86(2)	1(2)	37(2)	25(2)
O(9)	69(2)	72(2)	69(2)	2(2)	-25(1)	8(2)
O(10)	86(2)	127(3)	70(2)	-53(2)	-18(2)	35(2)

a The anisotropic temperature factor exponent takes the form: $-2\pi^2 (h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + \ldots + 2\ hka^*b^*U_{12})$.

TABLE 11. Hydrogen Coordinates, x 10^4, and Thermal Parameters, Å^2 x 10^3, for **21b** Form I.

Atom	x	y	z	U_{iso}/U_{eq}
H(4)	3345	1857	5522	55(10)
H(6)	2212	4764	6934	41(8)
H(8a)	2532	9334	5255	157(23)
H(8b)	2927	8975	4436	91(15)
H(8c)	3935	9183	5302	276(40)
H(11)	2493	8798	8360	57(10)
H(13)	-500	9316	6308	54(10)

TABLE 12. Anisotropic Thermal Parameters, Å^2 x 10^3, for **21b**, Form II.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N(1)	45(2)	29(2)	45(2)	-3(1)	14(1)	-5(1)
N(2)	45(2)	31(2)	45(2)	-3(1)	14(1)	-4(1)
N(3)	45(2)	79(3)	43(2)	6(2)	14(2)	10(2)
N(4)	67(2)	37(2)	63(2)	-9(2)	25(2)	-5(2)
N(5)	51(2)	56(2)	48(2)	7(2)	-2(2)	2(2)
N(6)	66(2)	45(2)	60(2)	-9(2)	12(2)	-21(2)
N(7)	63(2)	41(2)	59(2)	5(2)	-13(2)	-9(2)
O(1)	70(2)	101(3)	79(2)	8(2)	38(2)	-18(2)
O(2)	74(2)	95(2)	52(2)	-6(2)	27(2)	17(2)
O(3)	79(2)	38(2)	80(2)	-19(2)	17(2)	1(1)
O(4)	229(5)	71(2)	186(4)	-63(3)	172(4)	-77(3)
O(5)	66(2)	53(2)	92(2)	30(2)	2(2)	-3(2)
O(6)	104(3)	93(3)	117(3)	29(2)	-54(2)	-15(2)
O(7)	69(2)	71(2)	89(2)	-9(2)	6(2)	-35(2)
O(8)	113(3)	37(2)	138(3)	4(2)	-16(3)	-21(2)
O(9)	97(3)	71(2)	117(3)	12(2)	-43(2)	12(2)
O(10)	177(5)	62(2)	155(4)	-17(2)	-108(4)	-4(3)

a The anisotropic temperature factor exponent takes the form:
$-2\pi^2 (h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + \ldots + 2\, hka^*b^*U_{12})$.

TABLE 13. Hydrogen Coordinates, x 10^4, and Thermal Parameters, Å^2 x 10^3, for **21b** Form II.

Atom	x	y	z	U_{iso}/U_{eq}
H(4)	1525	5314	616	66(12)
H(6)	2357	8634	1300	49(10)
H(8a)	-294	8775	4621	122(19)
H(8b)	-1577	8558	3897	118(18)
H(8c)	-803	9642	3745	152(23)
H(11)	3634	11133	4379	73(13)
H(13)	1049	12434	2075	45(9)

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